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Evaluation of amine-blend solvent systems for CO_2 post-combustion capture applications

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Abstract

This work evaluates amine-blend solvent systems for CO_2 post-combustion capture applications for a 600 MWe conventional coal-fired power plant. The equilibrium-based Aspen Plus® absorption/desorption simulation tool was used for this evaluation. The total amine blends concentration was kept at the value of 30wt% for all different systems. Monoethanolamine (MEA) and diethanolamine (DEA) of weight variation of 3, 5, 10 and 15% are blended with 2-amino-2-methylpropanol (AMP), and methyldiethanolamine (MDEA). Fixed cross heat exchanger approach temperature of 10°C and stripper bottom temperature of 120°C are used as design specifications. These design specifications are used to screen each blend without CO_2 loading through sensitivity analysis. The AMP with 3, 5, 10 and 15wt% blended DEA (the activator) was found to require lesser reboiler duty in comparison with 30wt% MEA, with lowest value of 3.17GJ_{th}/tonCO_2 for 5wt% DEA activation. The promising four blends are further optimized using varying CO_2 loadings. The blend of 5wt% DEA and 25wt% AMP with lean loading of 0.07 mol_{CO2}/mol_{blend} requires the lowest reboiler duty of 3.03GJ_{th}/ton-CO_2 and lowest recirculation rate of 14.882m^3/ton. Absorber temperature profiles indicate temperature changes depend significantly on the lean loading. Stripper temperature profile shows that temperature swing is pronounced at the bottom, suggesting that CO_2 desorption takes place more at the lower stages.

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Keywords: Aspen Plus; Simulations; Amine blends; Post-Combustion Capture; Temperature Profile.

1. Introduction

Greenhouse gas control technology development is a major global effort at abating global warming [1]. Among these technologies, carbon capture and storage (CCS) is expected to play key roles in reducing CO_2 emissions from large stationary sources such as fossil-fuel-fired power plants, steel and cement industries. CCS option based on post-combustion capture (PCC) is particularly of interest due to its

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retrofit nature to existing plants, operational flexibility and adaptability to new plants [2]. Among the separation processes available for PCC, amine-based solvent chemical absorption is the preferred choice.

Reasons include its proven technology as applied in gas processing over decades [3] and high chemical affinity of alkanolamine for acid gases such as carbon dioxide and sulphur dioxide. Monoethanolamine (MEA) is the industrial standard alkanolamine for CO_2 absorption because of its fast kinetic rate of reaction, low density and viscosity. However, deploying the conventional 30wt% MEA-based process for large scale industrial application has been limited due to its high oxidative degradation, high corrosion rate, high absorption enthalpy, high energy penalty due to solvent regeneration and high capital cost [4]. However, tertiary amines such as methyldiethanolamine (MDEA) and sterically hindered amines like 2-amino-2- methyl-1-propanol (AMP) are known to have high cyclic capacity, low volatility and degradation, due to the bicarbonate reaction pathway. But they have slower kinetics when compared to MEA.

In other to obtain high performance solvent with higher CO_2 cyclic capacity, lower absorption enthalpy, lower solvent regeneration energy requirement, faster absorption kinetics with favourable environmental characteristics [5], a novel concept of blending various classes of these amines has been proposed and investigated [6, 7, 8, 9]. While several experimental and modeling efforts have been reported for solubility and absorption capacities for blends such as MEA/MDEA, DEA/MDEA and MEA/AMP, recent research interest is also considering diamine such as piperazine and cyclic monoamine such as piperidine and its alkanolamine derivatives [10, 11, 12, 13, 14, 15]. With the importance of process simulation as a connecting link between laboratory experiments and applications to pilot and demonstration plants, few simulation data are available in literature to compare modeling and experiments. Process flow optimization, process integration and process modification are identified as powerful tools that can be investigated in process simulation software such as Aspen Plus for detailed analysis [16]. In addition to the single solvents and solvent-blends, various flowsheeting process modifications such as flue gas precooling unit addition, split-flow configurations and combined heat exchanger-stripper configuration are analyzed in a research work [17].

In this work, the authors consider only the introduction of flue gas precooling unit, in an attempt to maintain the traditional flowsheet configuration for the purpose of evaluation. The purpose of this work is, therefore, to evaluate amine-blends with total composition of 30wt% using equilibrium-based Aspen Plus® absorption/desorption simulations. 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA), monoethanolamine (MEA) and diethanolamine (DEA) are considered. MEA and DEA of weight variation of 3, 5, 10 and 15% are blended with AMP and MDEA respectively.

2. Aspen Plus® Simulation Process Description.

Aspen Plus® version 7.3.2, commercial chemical engineering process software, is used for this work. Figure 1 provides the process flowsheet diagram. The flue gas composition is that of 600MW_e coal fired power plant as obtained in Abu Zahra dissertation [2], but with the removal of the sulphur dioxide and nitrogen oxides compositions based on the assumption that the flue gas has been pretreated in desulphurization and denitrogenation units respectively which also leads to flue gas cooling. The flue gas is compressed to accommodate pressure drop in the absorber. It is then isobarically precooled to conventional absorption temperature of 40°C. This is important for two reasons. It helps to condense water vapour from the flue gas before entering the absorber, which allows for overall water balance. The lowered temperature favors faster kinetics due to the exothermic nature of CO_2-amine-water reaction in the case of primary and secondary alkanolamine. In the absorber, the flue gas and the solvent mixture are

counter-currently contacted. The absorber is simulated through a 4-stage radfrac model, based on literature where it was established as the optimal equilibrium number of stages [18]. 10°C minimum temperature of approach is used as the cross heat exchanger design specification. The stripper is modeled with 8-stage radfrac Aspen plus model.

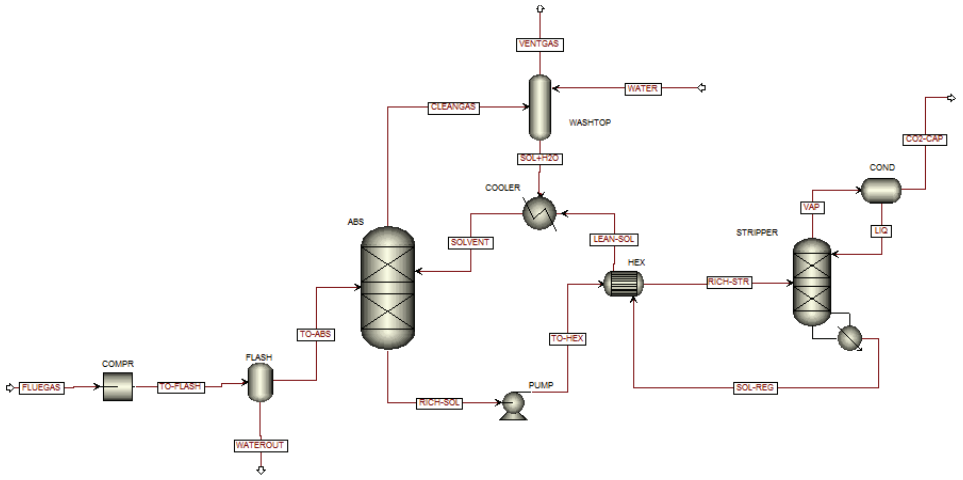

Figure 1: Aspen Plus Chemical Absorption Process Flowsheet Diagram with Precooling

The reaction pathway chemistry found in the software database is modified for each solvent blend by merging common pathways to eliminate degree of freedom conflicts in the reaction mechanism. The thermodynamic properties are kept as in the database. Sensitivity analysis is carried out for pure mixture of the blends under consideration with no CO_2 loading to determine the solvent circulation rate required. The authors use this approach because regenerating solvent by complete stripping of CO_2 implies higher energy penalty. Stripper bottom temperature of 120°C is set as the design specification. This is the typical low pressure steam temperature used for desorption. The obtained reboiler duty, the captured CO_2 molar purity and the molar recovery are evaluated for each solvent mixture.

3. Result and Discussion

The result is presented in Table 1. Thermal energy requirement for MEA process is reported to be about 4GJ/ton- CO_2 [19, 20]. Pure Solvent blends with thermal solvent energy requirement below 4GJ/ton- CO_2 are expected to be potential solvent candidates because optimizations with CO_2 loading will lead to lower reboiler duty as the expense of a higher solvent recirculation flow rate. Four mixtures satisfying this condition are presented in Table 2. For the loading simulations, total carbon dioxide balance is introduced as a design specification, in addition to total water balance. CO_2 recovery of 90% is used. Simulation data on the energy requirement, minimum solvent loading attainable, liquid-to-gas ratio, cyclic capacity and solvent rates under various solvent lean loadings are presented in Figure 2 to Figure **4** and Table 1 to Table 3.. DEA proves to be a good activating agent for both AMP and MDEA as shown in Table 1. With the four proportions in AMP performing better in terms of reboiler duty at no-loading when compared to no-loading MEA 30wt% base-case. The high regeneration level of 96% in the stripper is high at 94% purity on molar basis. DEA activation in AMP requires less energy due to its properties as a sterically hindered form of MEA, benefiting from the reaction kinetic properties of MEA chemistry and AMP molecular configuration which reduces energy penalty. MEA activation in AMP and MDEA show

significant energy requirement when compared to DEA. 3% MEA activation in 27% AMP requires 7.40GJ/ton thermal energy which is 233% more than the best of DEA (5% DEA activation in 25% AMP). Modified MEA/MDEA blend reaction mechanism predict to a lesser accuracy, going by the limit of solvent regeneration recorded. As the proportion of MEA activation increases, total solvent regeneration peaks at 74%. This implies that more energy penalty will be needed to strip the solvent to no-loading state. Also, it could be that the modified properties fail to predict the thermodynamic behaviour of all blends involving MEA as the activator.

From Table 2, as the lean loading increases from 0.1 to 0.4, the solvent rate required to achieve same CO_2 recovery increases by 268%, 312%, 292% and 354% for 3, 5, 10, 15% DEA activation in AMP respectively. 5% DEA activation in 25% AMP gives the highest cyclic loading of 0.474, 68% higher than reported values for 30wt% MEA and requires 24.25% less energy for solvent regeneration against a benchmark of 4GJ/ton. For all the blends in Table 2, Figure 2 shows the plot of the reboiler duty with CO_2 loading variations. The reboiler duty curve flattens out between 0.2 and 0.3 CO_2 loading. This could be due to a balancing out of the change observed in CO_2 stripping energy and sensible heat for water component. It is also clear from the table that the higher contribution of DEA (15wt%) resulted in higher energy requirement at the same lean loading as the other blends. The absorber stage temperature profile is given in Figure 3 for 5wt% DEA activation. The profile shows that as the lean loading increases, the temperature increase from the exothermic absorption reaction in the column decreases significantly. This is because of the increasing volume of solvent with lean loading. Figure 3 presents the temperature bulging resulting from the exothermic absorption. The return to lesser temperature at stage 1 and the observed bulging at stages 2 and 3 confirms the conclusion in literature that four is the optimum number of equilibrium stages for simulation.

Figure 4 shows the temperature profile in the stripper. It is observed that the temperature of the rich solvent entering the stripper at stage 3 remains fairly constant until it comes in contact with the low pressure steam at stage 8, except for cases of extremely low lean loading, like 0.07 for 5wt% DEA activation. This implies that the rich solvent receives most of the steam energy between stages 7 and 8 to meet the sensible heat, desorption enthalpy and stripping energy. So, as the steam rises in the column, its remaining sensible energy is sufficient to push up the desorbed CO_2 gas molecules. Above the feed stage, the temperature is observed to fall significantly. This is because of the cooled water from the condenser which washes down the steam and solvent with pure CO_2 leaving the top stage. Optimized 5% DEA/25% AMP simulation in this work is compared to optimized literature simulation data in . The blend shows better performance, requiring less reboiler duty even at higher CO_2 removal.

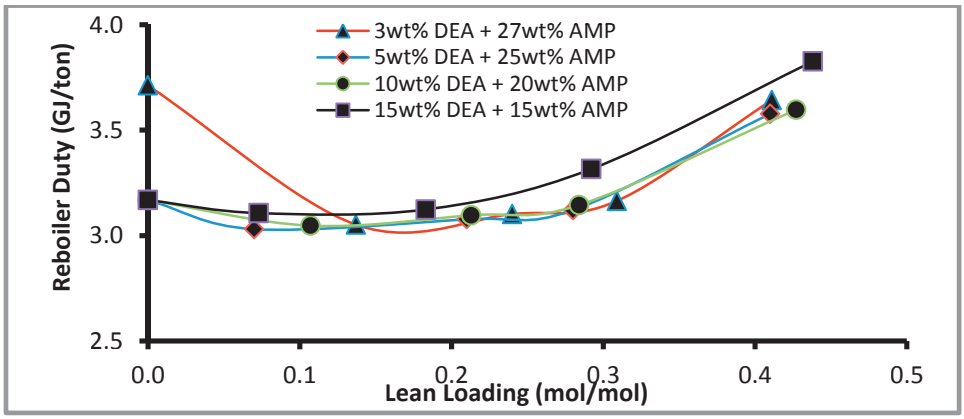

Figure 2: Reboiler duty vs. lean loading

Table 1: Sensitivity analysis for selected solvent blends

Solvent	Reboiler Duty (GJ/ton)	CO_2MolarPurity (mol/mol)	Loading(minimum) (mol/mol)
3% DEA+ 27% AMP	3.71	0.94	0.02
5% DEA+ 25% AMP	3.17	0.94	0.04
10% DEA+ 20% AMP	3.36	0.94	0.02
15% DEA+ 15% AMP	3.53	0.94	0.02
3% DEA+ 27% MDEA	4.36	0.92	0.03
5% DEA+ 25% MDEA	4.55	0.92	0.03
10% DEA+ 20% MDEA	4.00	0.93	0.03
15% DEA+ 15% MDEA	3.91	0.93	0.03
3% MEA+ 27% AMP	7.40	0.94	0.12

Table 2: Simulation result for promising solvent blends

Solvent	Loading (mol/mol)	L/G Ratio (mol/mol)	Solvent Rate (m^3/ton)	Cyclic Loading (mol/mol)
DEA 3%+ AMP 27%	0.137	3.883	17.782	0.387
	0.240	5.133	23.360	0.289
	0.309	6.269	28.410	0.235
	0.411	10.417	47.018	0.140
DEA 5%+ AMP 25%	0.070	3.220	14.882	0.474
	0.210	4.640	21.205	0.324
	0.280	5.616	25.539	0.265
	0.410	10.038	45.471	0.146
DEA 10%+ AMP 20%	0.107	3.551	16.329	0.438
	0.213	4.735	21.616	0.326
	0.284	5.777	26.234	0.265
	0.427	10.370	46.770	0.145
DEA 15%+ AMP 15%	0.073	3.409	15.662	0.471
	0.183	4.489	20.472	0.353
	0.292	6.771	30.650	0.242
	0.438	12.074	54.123	0.128

Table 3: Stripper Temperature Profile for DEA/AMP blends

DEA/AMP Blend		Stripper Stage Temperature profile (°C)							
	Loading	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
3/27wt%	0.137	86.68	88.51	92.37	92.62	93.09	94.54	99.50	110.43
	0.240	84.27	86.06	89.99	90.21	90.47	91.07	93.84	104.94
	0.309	82.08	83.82	87.82	88.04	88.27	88.66	90.51	101.18
	0.411	78.68	80.33	84.48	84.72	84.93	85.19	86.08	94.81
5/25wt%	0.070	88.01	89.86	93.63	94.07	95.16	98.28	105.29	114.66
	0.210	85.34	87.15	90.99	91.21	91.52	92.33	95.76	106.80
	0.280	83.45	85.22	89.11	89.33	89.57	90.07	92.43	103.32
	0.410	78.80	80.45	84.50	84.74	84.96	85.21	86.15	95.20
10/20wt%	0.107	87.77	89.61	93.21	93.53	94.28	96.48	102.32	112.31
	0.213	85.75	87.56	91.20	91.42	91.73	92.61	96.16	106.94
	0.284	83.91	85.69	89.37	89.58	89.82	90.35	92.85	103.65
	0.427	79.02	80.67	84.48	84.71	84.91	85.15	86.18	95.66
15/15wt%	0.073	89.02	90.87	94.28	94.77	96.00	99.17	105.76	114.61
	0.183	86.85	88.68	92.11	92.33	92.72	93.94	98.23	108.76
	0.292	84.35	86.14	89.62	89.82	90.04	90.51	92.80	103.26
	0.438	78.77	80.42	84.01	84.22	84.40	84.62	85.60	95.22

Table 4: Literature Comparison of simulation results

Parameter	Solvent (wt%)	Reboiler Duty	Solvent Rate	$\%CO_2$ Removal
This work	DEA/AMP	3.03	14.882	90
Douglas et al, 2005	30% MEA	4.00	-	85
Dave et al, 2009	30% MEA	4.17	18.36	86.5
	30% AMP	3.18	15.82	86.5
	30% MDEA	3.82	40.06	86.5

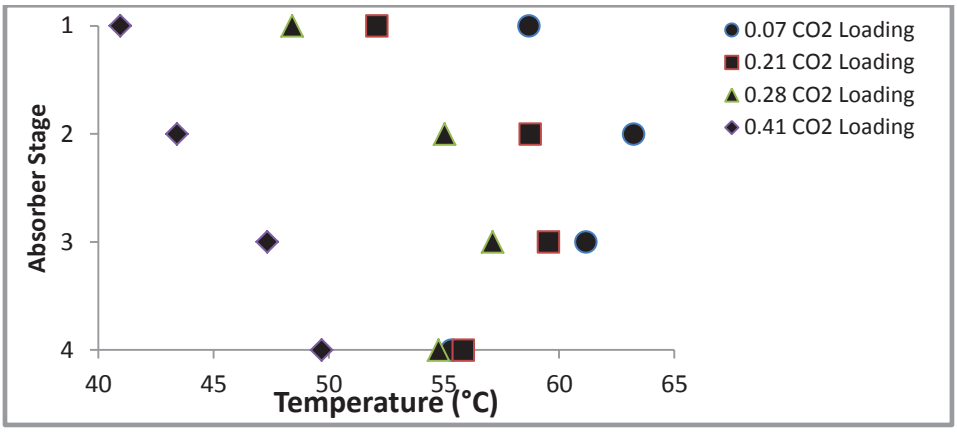

Figure 3: 5wt% DEA + 25wt% AMP Absorber Temperature Profile

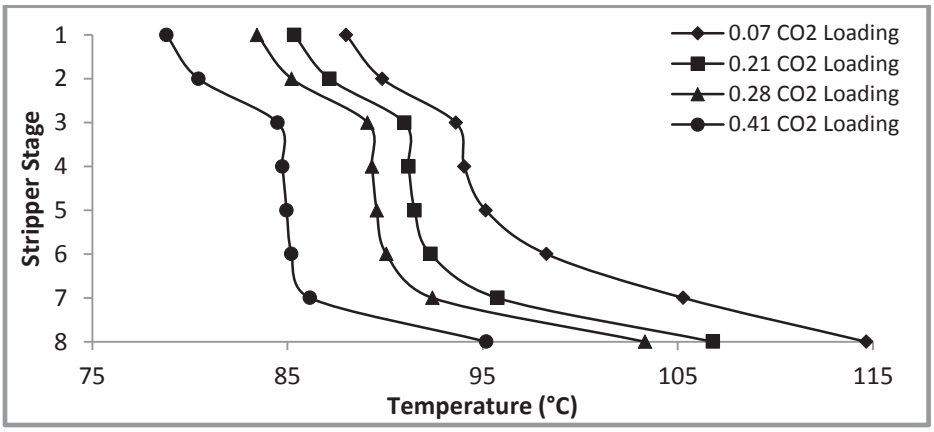

Figure 4: 5wt% DEA+25wt% AMP Stripper Temperature Profile

4. Conclusion

Equilibrium based CO_2 absorption simulation in 30wt% total mixtures of AMP and MDEA using DEA and MEA as activating agents is evaluated. DEA/AMP mixtures show lower energy penalty than any other mixture evaluated. 5wt% DEA/ 25wt% AMP mixture is of better performance in terms of reboiler duty, solvent rate and cyclic loading. The optimized lean loading of 0.7mol/mol, reboiler duty of $3.03GJ_{th}$/ton-CO_2 and lowest recirculation rate of $14.882m^3$/ton are recorded. In comparison to literature, DEA/AMP blends seem promising.

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